

FUNDAMENTAL ATOM CHEMISTRY - APPLICATIONS  
TO CHEMISTRY OF THE UPPER ATMOSPHERE

UNPUBLISHED PRELIMINARY DATA

FINAL TECHNICAL REPORT

Research Grant Nsg 158-61

P. Harteck

with

R. R. Reeves, Jr. and E. W. Albers

December 14, 1964

PO PRICE \$ \_\_\_\_\_  
OTS PRICE(S) \$ \_\_\_\_\_  
Hard copy (HC) 2.10  
Microfiche (MF) .50

FACILITY FORM 602

N65-17692 - N65-17695  
(ACCESSION NUMBER) (THRU)  
39  
(PAGES)  
CR-60442  
(NASA CR OR TMX OR AD NUMBER)  
(CODE)  
06  
(CATEGORY)

Rensselaer Polytechnic Institute  
Troy, New York

**Technical Status Report No. 5**

**FUNDAMENTAL ATOM CHEMISTRY WITH APPLICATIONS  
TO THE CHEMISTRY OF THE UPPER ATMOSPHERE**

764-18121  
10-12

**Rensselaer Polytechnic Institute  
Troy, New York**

**1 July 1963 - 31 December 1963**

**Research Grant NSG-158-61  
RPI Project 441.61**

**P. Harteck  
R.R. Reeves, Jr. and E.W. Albers**

As mentioned in the previous report the conversion data of tritium in the solid phase at 4.2°K and the conversion studies made at 27.2°K were submitted for publication in June 1963. This paper recently appeared in the Journal of The American Chemical Society; twenty-five copies are appended.

Investigation of the nitrogen system has continued using  $N_2^{14-14}$  and  $N_2^{15-15}$  under various conditions, but principally dictated by the knowledge gained from the tritium experiments. To date a small effect has been observed in the conversion of the nitrogen system at -1.5°K. From a continuing knowledge gained from the tritium experiments enhancement of this conversion appears likely.

The conversion of tritium in the heat conductivity cell now appears to occur exclusively via a wall catalysis; increasing the wall surface by a factor five resulted in a five-fold increase in the conversion rate. Although conversion in the gas phase undoubtedly still occurs, the contribution to the observed rate is negligible.

The half-lifetime for the conversion in the solid phase with varying amounts of hydrogen present (5% -50% hydrogen) varies linearly with the hydrogen content. Recently, the conversion of both isotopes in the solid phase has been measured simultaneously. Whereas the tritium half-lifetime increases with increasing amounts of hydrogen, the hydrogen half-lifetime decreases substantially.

#### Future Work

The role of ions in the solid phase conversion of tritium and tritium hydrogen mixtures still remains uncertain. Currently, a 10% tritium in hydrogen mixture is under investigation. If the rate of conversion of hydrogen increases substantially in the solid phase with 10% tritium present the conversion then is proceeding almost exclusively by an ion mechanism.

The problem of water vapor is being considered in connection with the noctilucent clouds as detailed by Dr. Hemenway of the Dudley observatory.

Fundamental atom and molecule reactions and their concomitant role in the chemistry of the upper atmosphere have been under investigation at RPI for the past ten years. These studies have been directed by Dr. Paul Harteck, Distinguished Research Professor of Physical Chemistry.

N65-17693

During the past three years under this grant we have investigated the kinetic processes associated with the following:

- (a) The ortho-para conversion of nitrogen and tritium.
- (b) The behavior of excited metastable nitrogen molecules ( $A^3\Sigma_u^+$ ) and the reactions of nitrogen atoms.
- (c) The chemiluminescent reactions suitable for upper atmosphere research: e.g., the reaction of sulfur, carbon disulfide, lead, bismuth and organometallic compounds reacting with oxygen atoms.

Under part (a) two papers have appeared in the literature and are appended. Work on the nitrogen atom chemistry under part (b) was included as a Ph.D. thesis topic, a copy of which is also appended. Two papers were published in this connection; reprints are given with the thesis. A portion of the study of chemiluminescent atom reactions, part (c), were reported earlier and a copy is also included here.

#### A. The Ortho-para Systems:

Bonhoeffer and Harteck in their classical experiments on the conversion of orthohydrogen into parahydrogen found that the rate of conversion in the solid phase, liquid phase and when the hydrogen molecule is adsorbed on charcoal exhibited rates of conversion which may be readily studied in the laboratory. Furthermore, as subsequently shown by Farkas and Sachsse the conversion of hydrogen in the gas phase while in the presence of a paramagnetic gas such as oxygen or nitric oxide could be followed conveniently also.

With the precise data available for hydrogen, the conversion of other molecular systems appeared feasible; such that, within a short period of time the conversion of paradeuterium into orthodeuterium was achieved by Harteck, Farkas and Farkas.

Although any homogeneous diatomic molecule with a non-zero nuclear spin exhibits ortho-para behavior, detectable enhancement of the low temperature modification will only occur in the region of 4.2°K and below. Consequently, the eventual isolation of a desired species requires special techniques.

Although tritium was investigated after an exhaustive series of experiments on the nitrogen system the paramount problems associated with the nitrogen system was not fully appreciated until we had successfully converted orthotritium into paratritium. Therefore, we have elected to discuss the tritium system first, since it offers a better point of departure for a discussion of the nitrogen system.

Using the heat conductivity method of Bonhoeffer and Harteck we have given evidence that it is possible to convert orthotritium into paratritium at low temperatures (liquid neon, 27.2°K, and liquid helium, 4.2°K).<sup>\*</sup> The rates of conversion were substantially faster for tritium than for hydrogen. From the theories of Wigner and others an estimate was made for the rate of conversion. Hydrogen and tritium follow the same statistics, and their nuclear magnetic moments are about the same (2.79 versus 2.98). If the conversion rates of hydrogen and tritium are compared according to theory, they should differ only by a factor three.<sup>\*\*</sup>

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<sup>\*</sup> For more complete details see appended reprints.

<sup>\*\*</sup> The comparison between ortho-parahydrogen and ortho-paradeuterium was not as conclusive because these two isotopes follow different statistics; in addition, their nuclear magnetic moments are significantly different (0.88 versus 2.79).

Two main reasons for this unexpected behavior seem plausible:

1. The smaller rotational quanta of tritium compared to that of  $H_2$  enhance the transition probability; in addition, at low temperatures the surrounding medium may absorb these smaller rotational quanta of energy released in the tritium transition ( $J = 1$  to  $J = 0$ ) much easier than in the hydrogen transition.

2. Ion-mechanisms may play an important role in the transformation under certain conditions.

From our present results we have not been able to determine in each case whether the ortho-para conversion is due to (1) a paramagnetic conversion or to (2) an ion-chemical mechanism:



and



The first reaction is a spin-reversal and the second is a chemical reaction over ions. It is well known that the paramagnetic conversion has practically no temperature coefficient for the conversion, but from other findings reaction (2) also has no detectable heat of activation.

The tritium we obtained was never completely free of impurities. In fact, a certain percentage of hydrogen was always present (the concentration of hydrogen was determined spectroscopically). In this connection a preliminary study showed that hydrogen acted as an inhibitor in the ortho-para conversion of the tritium. This find is obviously very interesting, viz., that the ortho-para conversion of one hydrogen species becomes hindered by another hydrogen species. We have made a series of hypotheses to explain

these phenomena, but additional research is necessary before a definitive answer may be elicited.

Furthermore, exploratory work has been made on a mixture of hydrogen and tritium which was equilibrated by a glow discharge to the high temperature equilibrium concentration of hydrogen tritide (HT). On cooling this mixture to low temperatures the chemical equilibrium was shifted quantitatively to the  $H_2 + T_2$  side; this equilibrium was established with a velocity comparable to the ortho-paratritium conversion, indicating that the same or a similar ion mechanism is operative.

Spectral plates of ortho-parahydrogen or ortho-paradeuterium do not exist in the literature, therefore we have made such spectrograms. (A copy of the hydrogen system is appended). We tried to make a similar spectrogram with ortho-paratritium, but we have been unsuccessful to date, even using the same apparatus which was used for the picture appended for hydrogen. From the existing theories such a spectrogram of the paratritium should have been readily obtained, since one would have expected a higher stability for the paratritium molecule than the parahydrogen molecule when exposed to a glow discharge. This rapid conversion in the discharge should be studied to clarify the mechanism for this transformation.

The rotational constant for nitrogen is  $1/30$  that of hydrogen. Consequently, any detectable enhancement of the ortho modification will not occur until a temperature of  $2^\circ K$  or lower is reached. The rate of conversion, however, may be extremely fast since below  $35.4^\circ K$  (the transition temperature for rotation in this solid lattice) the nitrogen molecules are hindered rotators; any conversion would only be likely at or below  $1^\circ K$ .

As we have indicated in our semi-annual reports prior to the tritium study a number of different avenues were tried but without success. (For details see appended reports). In every instance, however, we should emphasize the following:

(1) The extent of enhancement of the nitrogen system was determined spectroscopically from the intensity of the rotational lines within a given band produced by a glow discharge; we never observed a reverse effect and sometimes a minor indication.

(2) Secondly, a series of measurements were made such that half life times of a few minutes to five days would have been readily detected. From we know in the case of tritium, the rate of conversion of nitrogen should be much faster than expected.

(3) To date we have repeated a number of the nitrogen experiments of the first series in the light of the knowledge gained from the tritium system: again, only faint indications have resulted.

(4) It is possible also that the rate of the back conversion in the glow discharge may be extremely fast as it appears to be for tritium. Recent work, however, by Harteck, Dondes and Brown with  $N_2^{14-14}$  with  $N_2^{15-15}$  using ionizing radiation indicates that such a back conversion by an exchange process is unlikely.

#### (B) Metastable Molecules and Active Nitrogen-Hydrocarbon Reactions:

During the initial period of this general study it became evident that a mass-spectrometer with quantitative analytical capabilities was needed. A variety of uses within the experimental programs deemed the purchase of a CEC 21-130 virtually a necessity. Purity of gases and composition of gas mixtures for the ortho-para studies was of a paramount importance.



We incorporated a secondary entrance system to the analyzer which permitted a low pressure flowing gas stream to be continuously monitored by the mass spectrometer. By simply closing a valve we could use the system in the standard analytical fashion.

Through the past few years this mass-spectrometer was used to monitor a reaction study involving nitrogen atoms. The surface catalyzed excitation process was used with the active nitrogen to make excited molecules, and a variety of reactions were studied. An investigation was also made of the reactions between N-atoms and hydrocarbons.

This work also was supported in part by a NASA grant to RPI for Interdisciplinary Materials studies and constituted the thesis subject for a Ph.D. candidate, David R. Safrany. The work has been presented in detail in his thesis, and two publications have also appeared in the literature as a result of this work; copies of which are appended.

(C) The Chemiluminescence Reactions of Pb, Bi, CS<sub>2</sub> and Sulfur with Oxygen Atoms

At the request of Mr. Richard Hord of NASA's Langley Facility the chemiluminescent reactions of oxygen atoms with Pb, Bi, CS<sub>2</sub> and sulfur were studied in the 10-40 micron pressure range. The details of this work are contained in a report entitled "Studies for Chemical Releases in the Upper Atmosphere," requisite copies are appended.

Briefly, the chemiluminescent reactions of bismuth and lead gave luminosities which are an order of magnitude less than nitric oxide and consequently they would not appear to be suitable as release substances.

Carbon disulfide, sulfur or sulfur compounds may be used for chemical releases since these substances are free from a competing reaction with nitrogen atoms, which is not the case for nitric oxide.

Work on chemiluminescent reactions has continued with support especially from Air Force Cambridge. New results have been obtained which substantiate a two-body chemiluminescent reaction process which had been considered unlikely in recent years in view of the established three-body chemiluminescent processes also known. However, in the case of the low pressure nitric oxide-oxygen atom chemiluminescent reaction, our results clearly indicated that a simple two-body reaction mechanism dominates ( $\text{NO} + \text{O} \rightarrow \text{NO}_2 + h\nu$ ). (See appended reprint). In addition the sulfur monoxide-oxygen atom system also follows a simple two-body reaction mechanism in producing the chemiluminescence. The details of this work will appear in the near future in a paper accepted for publication in the Journal of Physical Chemistry.

# STUDIES FOR CHEMICAL RELEASES IN THE UPPER ATMOSPHERE

by

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Troy, New York

September, 1961

N65-17694

## INTRODUCTION

A survey type of study has been made at the request of NASA. This study was conducted to evaluate the proposal of Richard Hord for releasing bismuth and (or) lead in the upper atmosphere whereby a luminosity might be observed due to the reactions with oxygen atoms. In order to have a basis for comparison for the intensity of the luminosity observed, nitric oxide was also added to the O-atoms. Nitric oxide has been previously released in the upper atmosphere and reported in the literature.<sup>1</sup> Sulfur was also added since sulfur compounds are known to give a very strong luminosity in reaction with oxygen atoms.<sup>2</sup>

## Experimental Methods

A high vacuum system was used to study the reactions. The reaction vessel used was a 22 liter Pyrex glass flask connected to a mercury pump with a speed of about 50 liters per second under these conditions. The O-atoms were produced in a glow discharge and streamed into the flask (see appended colored slides and prints). The greenish white oxygen afterglow was just visible at the operating pressures used--in the order of 25 to 45 microns. In order to prevent the recombination of oxygen atoms on the walls, the flask was coated with ortho-phosphoric acid. Under these conditions the oxygen was estimated to be about 10% dissociated.

Both bismuth and lead were electroplated on to tungsten wire filaments. The metal could then be heated electrically by passing current through the tungsten filament. When visible radiation was first observed from the filament (600-700°C), the vapor pressure of

the bismuth or lead was sufficient to give a reasonable rate of vaporization (vapor pressures - Pb =  $1\mu$  at  $625^{\circ}\text{C}$ ,  $10\mu$  at  $718^{\circ}\text{C}$ ; Bi =  $1\mu$  at  $609^{\circ}\text{C}$ ,  $10\mu$  at  $698^{\circ}\text{C}$ ).

In the case of bismuth a whitish glow was observed; for lead a bluish glow was observed. Each glow persisted for approximately one hour with a total quantity of 200-300 milligrams of metal. The glow was not observed uniformly through the flask, but was strongest near the evaporating metals and toward the center of the flask.

Evaporation of both metals resulted in a coating of combined oxide and metal on the walls of the flask. This coating catalyzed the O-atom recombination on the surface, and in time the O-atom concentration within the flask was reduced to negligible amount. Eventually the vessel had to be recleaned.

Nitric oxide, being a gas, was simply added at a known rate to the O-atoms streaming into the vessel. Sulfur was added by placing powder in a combustion boat. The sulfur reacts rapidly at room temperature and is readily observed.

Photometric measurements were made with a 1P21 held a fixed distance from the vessel and directed at the maximum region of light emission. The results are given in the Table and are discussed in the next section.

**Table**  
**Estimated Light Emission for Substances**  
**Added to Oxygen Atoms at Low Pressures**

Substance	Total Pressure Microns	Partial pressure of substance cal- culated as BiO, PbO, SO, NO Microns	Estimated Total quanta emitted per second	Estimated total* quanta emitted per second per gram of sub- stance added
Bi	30	0.5	$8 \times 10^{13}$	$2 \times 10^{18}$
Pb	30	0.6	$5 \times 10^{14}$	$1 \times 10^{19}$
S	42	2.1	$3 \times 10^{16}$	$3 \times 10^{20}$
NO	24	3	$8 \times 10^{15}$	$2 \times 10^{20}$

\* Assuming the vapor of the added substance remains in the vessel for one second before being pumped out.

#### Results

To aid in evaluating these reactions, colored slides and photographs were made of the observed emission as well as spectrograms. A key for the various pictures is attached.

Bismuth Visually the chemical luminescence from the bismuth reaction with O-atoms appears white. It extends only a few centimeters from the filament or source of the bismuth vapor. The spectrogram showed banded structure typical of a diatomic molecule and the emission was assumed to be due to the excited BiO molecule.

The observed emission is about two orders of magnitude less intense than the emission from an equivalent amount of NO. This is estimated from the photometric readings taken.

Lead The lead gives a blue luminosity with O-atoms; apparently a continuum, since no discrete spectrum could be observed with the spectrograph. The intensity is considerably more than that for the equivalent amount of bismuth, but still an order of magnitude less than

that with NO. Again the luminosity did not fill the vessel but was concentrated near the center or the hot filament. Both lead and bismuth resulted in a deposit on the walls of the vessel.

Sulfur The sulfur is extremely easy to handle, since it reacts at room temperature and most remains in the gas phase. A coating eventually builds up on the wall, presumably due the formation of SO<sub>3</sub>.

It can be observed that the sulfur gave the highest luminosity as estimated from the photometric measurements. (The total pressure was slightly higher, but has little effect). The observed luminosity is a continuum and results obtained using a quartz system and quartz spectrograph show emission to be below 2400 Å.

Nitric Oxide The nitric oxide reaction is well known. The intensity of the luminosity observed is essentially equal to that calculated from the known reaction rates. These calculations indicate that approximately one NO molecule in every 100 added results in the emission of a photon or quantum of light.

#### Discussion

Under the conditions of these experiments it is probable that emission occurs by one of two basic mechanisms; first, a simple two-body reaction of the type



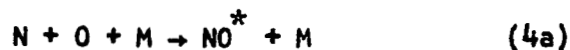
where the emission observed is a continuum. The second can be due to a simple three-body reaction of the type



where the emission is a band system of the AB molecule. Typical of reaction type (1) is:



Typical of reaction type (2) is:



where the emission is the  $\beta$ ,  $\gamma$  and  $\delta$  bands of NO.

In the case of bismuth, the band spectra are observed and hence the emission may be due to a three-body type reaction. The reaction with lead, however, appears to be due to a two-body reaction since a continuum is observed. The sulfur is also probably emitting due to a two-body reaction. The NO is known to be due to the two-body reaction.

In extrapolating to the upper atmosphere conditions, it should be considered that the three-body reaction decreases faster with decreasing pressure than a two-body reaction.

For two-body reaction

$$\frac{\text{Quanta}}{\text{second}} = k (A) (B) V$$

where  $k$  is the appropriate rate coefficient  
(A) and (B) are the concentrations of  
the reactants and  $V$  is the volume  
occupied by the reactants.

For the three-body reaction the third body concentration  $M$  must enter into the equation:

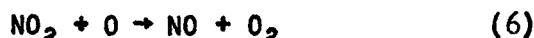
$$\frac{\text{Quanta}}{\text{second}} = k (A) (B) (M) V$$

If the bismuth is a three-body reaction and lead a two-body reaction, then the bismuth luminosity will decrease a factor 100 more than that of lead in extrapolating from a pressure of 30 microns to 0.3 microns total pressure.

These mechanism are not necessarily definitive. Others are certainly possible, but these appear reasonable.

The nitric oxide released in the upper atmosphere did not actually emit more than one photon per molecule released before the glow disappeared. However, it was possible that a chain mechanism

could sustain the NO whereby emission would be observed for some hours:

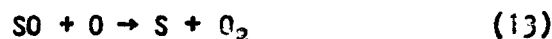
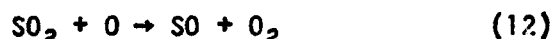
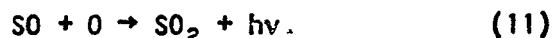
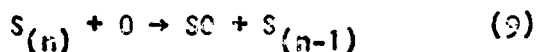


In the upper atmosphere, reaction (5) yielded the visible luminosity, reaction (6) was the very fast regenerating reaction for the NO, and reaction (7) was the parallel three-body reaction which was negligible at the low pressures.

The reaction was terminated by some interfering reaction, probably as suggested by Harteck<sup>(1)</sup>, by N atoms in the very rapid reaction:



In the case of bismuth or lead a similar chain mechanism may occur involving known oxides, but the experimental results here are not sufficient to indicate this. For NO it is known to occur, but in this particular arrangement, only 1 particle in 100 reacted to emit light and no catalytic process could be observed either. We suspect that sulfur will also go through a catalytic process via some mechanism. For example, any of the following reactions may be involved:



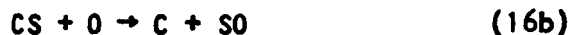
The sulfur system has been studied to a limited extent by our group and it is known that the N-atoms do not readily destroy the observed glow, as in the case of NO. Therefore, the emission from the reaction of sulfur with O-atoms in the upper atmosphere might well be intense and last for some time.



For simplicity  $\text{CS}_2$  might be released, where the same emission is known to occur. The reaction probably occurs, via:



or



The altitude of release for materials should be considered especially where the intensity of luminosity may be low and visual observation may be difficult. The original NO release was 106 KM and this is considerably above the maximum oxygen atom concentration which should be near 95 KM. The ratio of the O-atoms at these altitudes should be about 3. Therefore, a lower release should give considerably greater intensity.

A detailed discussion of the reliability of the present photometric measurements and estimates is not warranted in the light of the substances. Certainly the concentration of these constituents must decrease from the source to the wall because of diffusion to the wall where they are deposited. The photometric results may, therefore, be low.

#### Conclusions

(A luminosity does occur from the reaction of bismuth or lead with oxygen atoms. The luminosity from bismuth is conveniently located in the visible region--appearing white; and the luminosity is easily observed spectrographically as the emission has the band structure of  $\text{BiO}$ . However, lead is more intense and is observed easier photometrically.) The peak of the emission is in the blue. The lead may be emitting due to a two-body reaction, while the bismuth is via a three-body reaction. Therefore, the emission of lead may be an order of magnitude or more stronger in the upper atmosphere than that of bismuth. Our measurements indicate the intensity would still be an order of magnitude less than that with nitric oxide.)

It should be noted that the low vapor pressure of the bismuth and lead and the oxides results in a loss of reactant by simple diffusion to the wall. Consequently, the reactant concentration may be one-tenth or less than the calculated value where the reactant is considered to be removed by pumping only. Therefore, a release of bismuth or lead in the upper atmosphere may give better results than estimated by simple extrapolation from the values in the Table.

Sulfur may yield a very bright blue luminosity, also a continuum. (A release of  $\text{CS}_2$  might be easiest and gives equivalent results). This is suggested for consideration as a release material. It should be equivalent in intensity of emission to that from the NO release and may last longer because it is unaffected by N-atoms.)

#### References

1. Pressman, Aschenbrand, Marmo, Jursa and Zelikoff, *The Threshold of Space*, Pergamon Press (1957); Page 235.
2. P. Harteck and V. Kopsch, *Z. Phys. Chem.* B12, 327 (1931)

### Appendix

In this section we are including relevant slides and prints. An alpha reflex camera was used with indoor type high-speed Ektachrome film at f 2.8. Further details for individual photographs are reported in the key. The corresponding slides and prints may be identified from the Roman numeral on each.

**Key for Slides and Prints for the Reactions of Oxygen Atoms  
With Bismuth, Lead, Sulfur, and Nitric Oxide**

Number	Designation	Exposure Time in seconds	Distance to Flask in feet	Background light
I	Vacuum System	--	--	--
II	Bi	120	10	on
III	Bi	120	10	off
IV	Bi	120	10	on
V	Bi	10	4	off
VI	Bi	30	4	off
*VII	Bi	30	4	off
VIII	Pb	120	10	off
IX	Pb	120	10	on
X	Pb	30	4	off
XI	Pb	30	4	on
*XII	Pb	30	4	on
*XIII	Pb	120	4	on
XIV	S	30	10	on
XV	S	120	10	on
XVI	S	120	4	on
XVII	S	30	4	on
XVIII	NO	30	10	on
XIX	NO	120	10	on
XX	NO	10	4	on
XXI	NO	120	4	on
XXII	NO	30	4	on

\*These photographs were taken at higher rates of evaporation.

Technical Status Report No. 1

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Rensselaer Polytechnic Institute  
Troy, New York

1 July - 31 December 1961

Research Grant NSG-158-61  
RPI Project 441.61

P. Harteck  
and  
R. R. Reeves, Jr. and E.W. Albers

In this period, two projects have been conducted simultaneously: (1) an investigation of the reactions of oxygen atoms with bismuth and lead (in comparison with the reactions of oxygen atoms with nitric oxide and carbon disulfide); and (2) an investigation of the separation of ortho-para type systems.

The former project has been reported and sent to NASA<sup>(1)</sup>. Essentially, the report contains measurements of intensity for the luminosity produced in the above cases along with limited spectral results.

The second project has been concentrated on the conversion of molecules of the ortho-para type into the lower state, analogous to the transformation of ortho-para hydrogen into para-hydrogen by the use of a suitable catalyst at low temperatures. For this work nitrogen and methane were selected and each have been studied in detail.

In case of nitrogen the conversion is difficult because nitrogen does not normally rotate freely below 35.4°K. Experimentally, nitrogen mixed with inert gases as diluents, was cooled to the temperature of liquid helium (4.2°K) and below. These mixtures were preabsorbed on a catalyst. The catalysts were selected on the basis of their paramagnetism and ranged from charcoal with a relatively low value to the intermediate and high values exhibited by the rare earth oxides. The result of each experiment was determined spectroscopically by looking at the variation in intensity of the rotational structure of the molecule in the second positive system and of the ion in first negative band system. To date no substantial change has been observed.

For a polyatomic molecule such as methane, three variations are possible; viz., ortho, para, and meta. Although this complicates the analysis, the higher rotational constant of methane may simplify the experimental procedure; i.e., a measurable separation may be made at 4.2°K.

(1) "Studies For Chemical Releases in the Upper Atmosphere", R.R.Reeves, E. W. Albers and P. Harteck. Sent to Mr. Richard A. Hord, Dynamic Loads Division National Aeronautics and Space Administration, Langley Research Center, Langley Air Force Base, Virginia

Furthermore, the heat capacity data of Euchen<sup>(2)</sup> on mixture of methane and krypton indicate that methane is still freely rotating at the temperature of liquid helium. In this work a mixture of methane and krypton was brought into contact with a number of the same catalysts used for the nitrogen system. Again, results were determined by spectroscopic means by looking at the rotational structure of methane's two active infrared bands; results so far have been negative.

#### Future

Future work will continue the studies of luminescent reactions; possible rocket shots are now planned. The objectives of wind measurements are associated with chemiluminescent reactions. It is suggested that a single rocket with a payload of different materials be considered as a survey means; i.e., at successive intervals a different material could be ejected thereby establishing the most suitable substance by the cheapest means.

Work will continue also on the ortho-para systems. In order to obtain information on molecules with lower rotational constants, e.g., methane and nitrogen, we now plan to look at ortho-para tritium as a guide to the more difficult and complex nitrogen and methane molecules.

(2) A. Euchen and H. Vieth, Z.physik Chem. B34, 275 (1936).

**Technical Status Report No. 2**

**FUNDAMENTAL ATOM CHEMISTRY WITH APPLICATIONS  
TO THE CHEMISTRY OF THE UPPER ATMOSPHERE**

**Rensselaer Polytechnic Institute  
Troy, New York**



**1 January - 30 June 1962**

**Research Grant NSG-158-61  
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R.R. Reeves and E.W. Albers**



The study of releases of chemicals in the upper atmosphere has been continued. This work is closely allied with work with AFCRL under Dr. N.W. Rosenberg. In particular, our laboratory results have indicated that  $\text{CS}_2$  should react with O-atoms to give a substantial glow in the chemosphere in the 100-120 kilometer region. Mr. Richard Hord of NASA\* has been instrumental in having the  $\text{CS}_2$  released. The results were unfortunately negative, yielding no emission. Several reasons are possible for no emission, but at present it appears most likely to us that the  $\text{CS}_2$  was not actually released. This question should be resolved in the near future, since Mr. Hord has informed us that a new release is planned in September.

In connection with work for Cambridge and at the suggestion of Dr. Rosenberg and his group, we have studied the reaction of trimethyl aluminum (TMA) with O-atoms. The purpose of this study is to try to obtain more information on the results of grenade experiments in Australia reported by Woodbridge, where, for a very small weight, less than one pound, a reasonably persistent glow was obtained in the night sky, apparently through a reaction involving oxygen atoms and some substance involved in the grenade experiment. One of the major elements in the grenade was aluminum and hence it was thought that free aluminum might be released in the explosion and yield this luminosity by some mechanism. Our laboratory results indicated a bright glow from the TMA and O-atom reaction where we assume the aluminum is the main reaction species from the TMA. At present, however, we do not believe the intensity is sufficient to cause the observed luminosity from the grenades, although many experimental difficulties prevent an accurate evaluation. The best evaluation of the results, indicates that an overall intensity from this reaction would be equivalent per unit weight to the reaction evolving nitric oxide and have a very similar spectral distribution to the radiation.

\*

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The glow from these grenade experiments has been a point of discussion with Mr. Hord and NASA.

We would like to point out a possible alternate luminosity source which we consider quite possible. This is the reaction of N-atoms with molecular oxygen. If N-atoms are present in the ambient where the grenade is released, the resultant shock wave, on passing through the atmosphere, will accelerate the  $N + O_2 \rightarrow NO + O$  reaction, resulting in a relatively high level of nitric oxide which can cause the luminosity observed. An ambient nitrogen concentration of  $10^9$  atoms per cubic centimeter is sufficient to readily produce such a glow; this is still considered a not unreasonably high nitrogen-atom concentration despite some lower "upper limits" now claimed.

The work on ortho-para systems has continued. We have now converted normal tritium to paratritium; this work will be reported in the literature shortly with appropriate distribution to NASA. The tritium was converted using a coconut charcoal catalyst in the 8 to 20°K range, measuring the degree of transformation with usual thermal conductivity technique. Half time for the conversion was four to five minutes. There was no observable effect from the radioactive nature of the tritium with regard to an autocatalytic conversion. This transformation is expected to be especially useful in obtaining pertinent information for experimental techniques for transforming the nitrogen or methane systems to their lower states.

We have purchased a mass spectrometer on this grant to use in connection with reaction studies of excited molecules. This work is just getting underway with the construction of the equipment just coming to completion. The mass spectrometer is also being used regularly for the entire project, for standard chemical analysis and for testing for purity of various gases.

In the immediate future we plan to continue the study of O-atom reactions associated with the upper atmosphere. This work will be at

3.

a somewhat reduced level as we place more emphasis on the ortho-para systems. The study of reactions of excited molecules with various ground state molecules should begin during the latter part of July with the completion of the apparatus. •

**Technical Status Report No.3**

**FUNDAMENTAL ATOM CHEMISTRY WITH APPLICATIONS  
TO THE CHEMISTRY OF THE UPPER ATMOSPHERE**

**Rensselaer Polytechnic Institute  
Troy, New York**

**1 July 1962 - 31 December 1962**

**Research Grant NSG-158-61  
RPI Project 441.61**

**P. Harteck  
and  
R.R. Reeves, Jr. and E.W. Albers**

Precise kinetic data for the conversion of 3:1 ortho-paratritium into 1:1 ortho-paratritium on a coconut charcoal at liquid neon temperature have been obtained. The publication of these data will appear in Zeitschrift fur Naturforschung in March 1963. (Twenty-five copies of this manuscript were forwarded to NASA in November 1962).

The half-lifetime for the conversion at 27.4°K (liquid neon) was found to be one minute; back conversion on the same coconut charcoal at the temperature of liquid nitrogen (77.4°K) gave a half-life of 0.92 minutes. For hydrogen under identical conditions the half-lifetime was twenty-four times slower. To a first approximation the magnitude of the difference between hydrogen and tritium results in a factor of eight when one considers the transition probability expression derived by Wigner<sup>(1)</sup> for the homogeneous conversion in the gas phase. This marked variation between hydrogen and tritium is a most striking and interesting result and deserves further investigation. In this connection the effect of ions in the gaseous and solid state is now being studied.

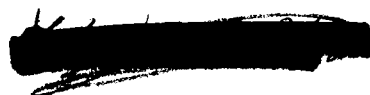
Currently we are engaged in establishing the kinetics for the following: conversion of tritium in a solid lattice containing hydrogen; back conversion of paratritium (1:1) ortho-paratritium mixture in the presence of nitric oxide at room temperature, which is an independent measure of the nuclear magnetic moment; half-lifetime of conversion for pure tritium at the temperature of liquid helium; and the conversion of tritium on silica gel.

Preliminary results indicate a half-lifetime of 100 minutes for the mixture of hydrogen and tritium in the solid state. For the homogeneous back conversion of tritium in the presence of nitric oxide the measured half-lifetime was 17 minutes; this result agrees with the data reported by Farkas<sup>(2)</sup> for hydrogen back converting under similar conditions, allowance being made for the change of mass as required by the transition probability expression

**Technical Status Report No. 4**

**FUNDAMENTAL ATOM CHEMISTRY WITH APPLICATIONS  
TO THE CHEMISTRY OF THE UPPER ATMOSPHERE**

**Rensselaer Polytechnic Institute  
Troy, New York**



**1 January 1963 - 30 June 1963**

**Research Grant NSG-158-61**

**RPI Project 441.61**

**P. Harteck  
R.R. Reeves, Jr. and E.W. Albers**

of Wigner. Measurements related to the solid phase conversion and conversion on silica gel are in procedure.

At the Spring Meeting of the American Chemical Society in March 1963 a second paper on the tritium system will be presented and published in Journal of the American Chemical Society. Prior to this time the requisite copies of this paper will be forwarded to NASA.

Future work will be directed toward establishing the effects of the ions produced by the radioactive decay of tritium on the mechanism of conversion for the homogeneous and heterogeneous phases. In the future after completing our experimentation on ortho- and paratritium we plan to conduct exploratory experiments on ortho- and para  $N^{14}$ - $N^{14}$  and  $N^{15}$ - $N^{15}$  and on the three methane systems. We hope that the knowledge acquired with the ortho- and paratritium experiments will help us to make a successful approach to this very tempting but experimentally difficult field.

#### Literature

Copies of papers discussed at the Informal Conference on Photo-chemistry in Brussels in June, 1962 are attached. This work was supported in part by this grant.

#### References

- (1) E. Wigner, Z. f. physikal. Chemie, B, 19, 203 (1932).
- (2) A. Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen", Cambridge Univ. Press, 1935.

The rates of conversion of tritium in the solid phase at 4.2°K (liquid helium) and the gas phase at 27.2°K (liquid neon) have been measured. These data have been submitted for publication in The Journal of the American Chemical Society. (Twenty-five copies of this manuscript were forward to NASA in June 1963).

The measured half lifetime for the conversion of tritium in the solid phase was found to be seventeen minutes. This rate of conversion is 210 times faster than for normal hydrogen. The enhanced rate of conversion of tritium, however, may be due entirely to a more favorable energy transfer process. Examination of the measured half lifetimes for hydrogen, deuterium and tritium in the solid phase seems to indicate that for tritium a one phonon process is very likely whereas for hydrogen the minimal energy process must involve two phonons. Deuterium, however, may be either a one phonon or two phonon process.

For the gas phase conversion at 27.2°K variation of the amount of bare metal surface within the heat conductivity cell envelope markedly changes the half lifetime for the gas phase conversion. Since the heat conductivity cell remains immersed in liquid neon, it is likely that ions play a major part in the conversion in the gas phase.

#### Future Work

Since the role of the ions may be of prime importance in the solid conversion, we plan to study in great detail the conversion of hydrogen-tritium mixtures and possibly deuterium-tritium mixtures. For the effect of ions on the gas phase conversion the pressure of tritium will be increased from one millimeter to six millimeters. Since it appears that the rate of conversion should vary with the third or fourth power of the pressure if the conversion takes place over ions in the gas phase, one should only be able to measure the 1:1 ratio of ortho-paratritium at 27.2°K.



CHEMILUMINESCENT REACTIONS OF MAJOR  
IMPORTANCE FOR THE UPPER ATMOSPHERE\*

by

Paul Harteck

and

R.R. Reeves, Jr.

N65-17695

Rensselaer Polytechnic Institute  
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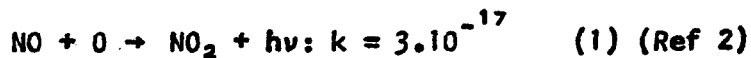
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The release of nitric oxide in the upper atmosphere six years ago by Dr. Zelikoff and his group<sup>(1)</sup> gave striking evidence for the existence of the chemosphere and particularly the relatively high concentration of oxygen atoms in this region. This paper discusses some considerations and laboratory experiments we have made concerning possible chemical releases and their effect on the upper atmosphere, and also what information might be obtained in this way about the nature of the upper atmosphere.

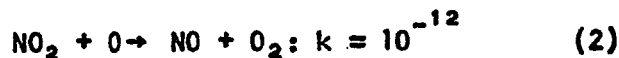
*Author*

The solar radiation has an intensity which is a maximum in the visible region around 5000 A. In the upper atmosphere regions where the total pressure is one micron or less, one need consider only radiation which has a very high absorption coefficient. Radiation below 1800 A is absorbed by oxygen in this region to form O-atoms. Still lower wavelengths starting about at Lyman  $\alpha$  (1216A) can make both ionization and dissociation processes in the atmosphere. This sum of effective radiation is less than a per mil of the total energy of solar radiation.

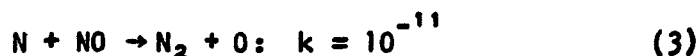
This release of NO by Dr. Zelikoff and his group at about 106 km gave a luminosity which was almost exactly what was predicted. The nitric oxide reacts with O-atoms giving the well-known reaction:



which may be followed by



The luminosity resulting from the NO release was readily observable indicating the presence of O-atoms. If the O-atoms had a concentration of  $1-3 \times 10^{12}$  particles per cubic centimeter, then there would be one photon emitted per NO molecule by reaction (1) in every few hours. Actually, however, the glow disappeared in a fraction of an hour and at the time we speculated that this could be due to nitrogen atoms via:



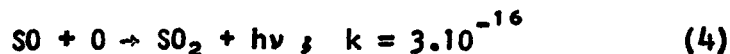
This idea that the N-atoms might be in sufficient concentration to interfere has not been widely accepted.

We have been looking for other chemicals to release which might give:

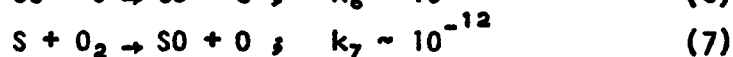
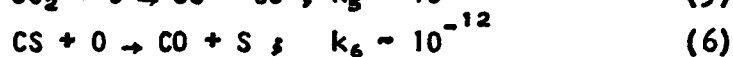
- 1) more luminosity (per pound)
- 2) avoid destruction by N-atoms (or other loss mechanism)
- 3) indicate the N-atom concentration

When considering ways to have a more intense luminosity the question also arises as to what is the amount of energy stored as dissociation energy in the upper atmosphere and what is the number of light quanta which could be emitted in a process which emits one light quanta in the visible for each O-atom or for each pair of O-atoms. Assuming a maximum O-atom concentration in the 100 km altitude region of  $10^{12}$  particles per  $\text{cm}^3$ , and a scale height of  $10 \text{ km} = 10^6$ , we see that, per  $\text{cm}^2$ ,  $10^{18}$  O-atoms are present during the night. By recombination, these  $10^{18}$  O-atoms could release an energy equivalent of  $0.1 \text{ cal/cm}^2$ . Since the sun radiates about  $10^{17}$  light quanta in the visible, the O-atoms stored in the upper atmosphere are sufficient, if an adequate chemical reaction could be found, to emit for a few seconds a light intensity equivalent to the luminosity of the sun during daytime. Obviously this high intensity - short duration emission is not practical to achieve. It is well in the realm of possibility, however, to release substantial amounts of a chemical with rockets in the regions where the O-atoms are most abundant and thereby induce photochemical reactions over wide areas. The emission may be sufficient to be easily seen from the ground, or even to brighten the night sky for several hours to a degree more than that of a full moon (more than  $10^{12}$  light quanta per centimeter square per second).

I remember from over thirty years ago when we had been first studying reactions with oxygen atoms, that hydrogen sulfide gave a beautiful intense blue emission.<sup>(4)</sup> This glow is also readily observed with the reaction of O-atoms with sulfur, carbonyl sulfide, and carbon disulfide. A release of such a chemical might give a high intensity of light via:



For CS<sub>2</sub> we have studied the reaction and it probably follows a multi-step oxidation at these low pressures:



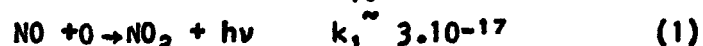
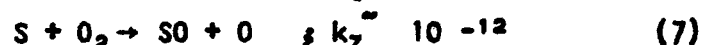
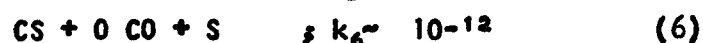
Reactions (5-7) appear to be fast with efficiencies of 10<sup>-3</sup> or better while reaction (4) may be 10<sup>-6</sup> or better. The coefficients indicated are estimated from preliminary work at room temperature from 100 microns down to 5 microns.

Reactions (5-7) consume rapidly O-atoms without light emission. Therefore a release of CS<sub>2</sub> in the upper atmosphere may yield a dark center with a bright blue shell which would grow with time. Unfortunately, there can be no regeneration of the SO via



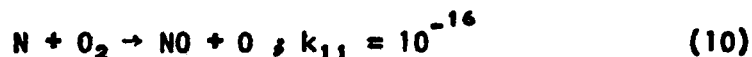
It might be well at this point to compare the relative intensities of SO emission resulting from reaction (4) and NO emission from reaction (1). It is true that NO may be regenerated by reaction (2), while SO is not regenerated by reaction (8). The reaction rate of NO is, however, small ( $k = 3.10^{-17}$ ) compared to that from SO ( $k = 3.10^{-16}$ ). Furthermore, the NO<sub>2</sub> produced by reaction (1) is apparently not available for regeneration because of reaction with N-atoms. Therefore, the release of a sulfur compound should give a substantially brighter luminosity.

Because of the possible interference of N-atoms in the nitric oxide release, we decided to investigate the mixed N-atom-O-atom reaction with sulfur compounds. We have tried the effect of N-atoms with a mixture of carbon disulfide and O-atoms and it not only doesn't interfere, it can actually enhance the total emission via the following reactions:\*



The blue emission from (4) is not only enhanced by the production of O-atoms from N-atoms via Reactions (9) and (7), but also the color may change to yield a more whitish glow with time due to light emission by reaction (1). This effect was readily observed in the laboratory. Reaction (9) should be of basic importance for a sulphur or NO plus sulphur release in the upper atmosphere since the SO will have the effect to destroy the N-atoms and hence the resulting NO may have a substantial longer lifetime at least near the center of the release.

The role of N-atoms in the upper atmosphere is not entirely clear because of the lack of direct experimental evidence for the concentration and duration in the upper atmosphere. The N-atoms should have a lifetime of some hours at 100 kilometers (3) if they were consumed only by the reaction:



Glow observed from the grenade releases may<sup>(5)</sup> be due to a shock wave which would accelerate reaction (10), with the subsequent reaction of NO with O-atoms in reaction (1).

\*These reactions have been studied by Dondes and Liuti in detail. This work is being prepared for publication.

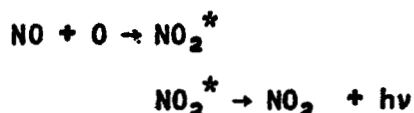
There arises the interesting problem of what other substances could be considered for such releases and what properties they should possess. Since the release of these substances will take place at very low pressures O-atom concentrations are highest, it would be preferred to have two-body reactions, since three-body reactions may be neglected. The two-body mechanism may be of two types:



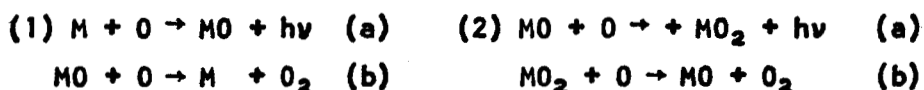
and



At present we don't know any reactions of Type I involving O-atoms which would emit light in the visible with a high efficiency. We are therefore limited to Type II. To this group belongs reaction (1), which can be written in the form as above as:



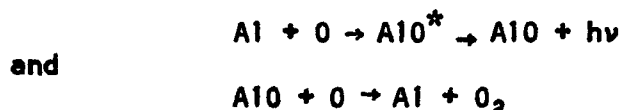
Other representatives of this type of substance which have to be considered are metals release directly, or as metal organic compounds, or as volatile inorganic compounds. Unfortunately these reactions are difficult to study and simulate in the laboratory, because usually metal oxides are formed which will deposit on the walls of the vessel and catalytically destroy the O-atoms. The ideal metal could behave in two ways:



The light emission should be in the region where the eye is most sensitive and the MO or MO<sub>2</sub> should not undergo a chemical reaction with N-atoms which stops the chain. To properly investigate these types of reactions, we would need a very large reaction vessel, so that the wall effects would become reduced. We made all our experiments in a reaction vessel of 50 liters at about 10-20 micron pressure. This pressure is

about by a factor 100 lower than most experiments which are performed with atoms generated with a glow-discharge, but still a factor 10 higher than the pressure in the chemosphere. We would like to emphasize, that under our experimental conditions we come nearer to the condition which prevail in the chemosphere, than most of the experiments performed on these lines.

We investigated a series of the metal organic compounds (6). From these substances  $\text{Al}(\text{CH}_3)_3$  gave, with O-atoms, a most beautiful white luminosity. In the figure can be seen the spectrum of light emitted. The dissociation energy of  $\text{AlO}$  is quoted as  $D_0 \sim 3.75$  volts in G. Herzberg, Spectra of Diatomic Molecules, 1951. This dissociation energy would be in line with the observed spectrum which extended to about 3800 Å. A chain reaction (5) is therefore possible via:



This would fulfill both properties which one would desire for a chemical substance for release, namely a luminosity which is predominantly in the visible, and also a chain mechanism to regenerate the reactant.

At present we are designing an experimental arrangement which can extend the work still lower pressures to more nearly simulate the Chemosphere.

The authors wish to acknowledge the assistance of Dr. L.G. Bassett in preparing this paper.

This work was supported in part by the Electronic Systems Division, Air Force Systems Command, USAF, AF Office of Scientific Research, and the National Aeronautics and Space Administration.

References:

1. Marmo, Pressman, Aschenbrand, Jursa, and Zelikoff; "The Threshold of Space", Pergamon Press, 1957, p. 235.
2. A. Fontijn and H.I. Schiff; "Chemical Reactions in the Lower and Upper Atmosphere" Interscience Publishers (Wiley), 1961, p. 239. (Although there seems to be some doubt if the light emission is directly by this two-body reaction, we still favor this in preference to a three-body complex mechanism).
3. The values for rate coefficient pertinent to many upper atmosphere reactions are tabulated in a previous paper, P. Harteck, and R.R. Reeves, "Chemical Reactions in the Lower and Upper Atmosphere" Interscience Publishers (Wiley), 1961, p. 219.
4. P. Harteck and U. Kopsch Z. physik Chem., B12, 327 (1931).
5. D.D. Woodbridge; "Chemical Reactions in the Lower and Upper Atmosphere" Interscience Publishers (Wiley), 1961, p. 373.
6. We like to acknowledge that the experiments with metal-organic compounds were prompted by discussions with Drs. N.W. Rosenberg and D. Galumb of Air Force Cambridge Research Laboratories.

Chemical Reactions of Excited Molecules\*

Robert R. Reeves, Jr. and Paul Harteck

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ABSTRACT

The excited molecules are produced by use of a surface catalyst. The chemical reactions of the nitrogen excited molecules ( $N_2A^3\Sigma_u^+$ ) with different substances are discussed along with the reaction of the excited oxygen molecule ( $O_2A^3\Sigma_u^+$ ) with oxygen and nitric oxide. The interaction of highly vibrationally excited OH radicals is also discussed.

\* Discussed at the Informal Conference on Photochemistry  
at the University of Brussels, June 1962

Abstract will appear in the Bull. Soc. Chim. Belg. Spring 1963